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HETEROGENEOUS IGNITION THEORY

10-865137

by

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Research Department

ABSTRACT. Mathematical solutions are obtained for a model of solid propellant ignition by the combined action of external flux and surface reaction between a solid fuel and gaseous oxidizer with hypergolic ignition as the limiting case. Several commonly used definitions of ignition are examined and compared in the light of the surface temperature history. Conditions are established under which the definition of ignition can be expected to influence ignition time; major differences appear at high heating rates between the ignition times based on constant ignition temperature and on other criteria. The effect of oxidizer concentration on ignition time is investigated; at low pressures, the manner of variation of concentration is unimportant, while at high pressures, variations of mass fraction and pressure have different effects. Finally, it was found that chemical kinetics is the principal factor in determining ignition time, while mass diffusion rate imposes a limit on the attainment of ignition without significantly affecting ignition time.



NAVAL WEAPONS CENTER  
CHINA LAKE, CALIFORNIA \* FEBRUARY 1970

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### FOREWORD

This report was prepared as part of a research program at the Naval Weapons Center on the subject of Ignition of Solid Propellant Rockets, sponsored under Naval Ordnance Systems Command Task Assignment ORD-331-001/200-1/UR0-100-202.

In a previous report (NAVWEPS Report 8987, NOTS TP 3954), the then current status of the solid phase, heterogeneous, and gas phase theories of solid propellant ignition was summarized. Following this, an extended analysis of solid phase theory was published as NWC TP 4618. The present report examines the ignition characteristics of a solid material under the influence of external heating and surface reaction with a gaseous atmosphere.

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CONTENTS

Nomenclature . . . . .	iv
1. Introduction. . . . .	1
2. Mathematical Model. . . . .	1
3. Qualitative Behavior. . . . .	4
4. Solution and Results. . . . .	7
5. Relevance to Propellant Ignition. . . . .	10
6. Interpretation and Implications of Results. . . . .	14
7. Summary . . . . .	22
References. . . . .	24

NOMENCLATURE

B Chemical rate coefficient ( $\text{gm}/\text{cm}^2\text{sec}$ )  
C Specific heat ( $\text{cal}/\text{gm}^{\circ}\text{K}$ )  
D Coefficient of mass diffusion ( $\text{cm}^2/\text{sec}$ )  
E Activation energy of surface reaction ( $\text{cal}/\text{mol}$ )  
 $K_1, K_2, K_3, K_4$  Constants (Eq. 29, 30)  
M Molecular weight  
Q Heat evolved in surface reaction ( $\text{cal}/\text{gm}$  of oxidizer reacted)  
R Universal gas constant ( $\text{cal}/\text{mol}^{\circ}\text{K}$ )  
T Temperature  
 $T_o$  Surface temperature at instant of contact between gas and solid phases (Eq. 27, 28)  
Y Mass fraction of oxidizer  
a Empirical constant (Eq. 21)  
b Empirical constant (Eq. 24)  
h Specific enthalpy ( $\text{cal}/\text{gm}^{\circ}\text{K}$ )  
n Order of surface reaction with respect to oxidizer  
p Pressure ( $\text{dyne}/\text{cm}^2$ )  
q Flux density of external energy ( $\text{cal}/\text{cm}^2\text{sec}$ )  
t Time (sec)  
x Distance (cm)

- a Diffusion parameter ( $a = \Gamma T_0 / \rho_1 D^{1/2} Q Y_0$ ), dimensionless
- b Activation energy parameter ( $\beta = E/RT_0$ ), dimensionless
- y External heating parameter [ $\gamma = q \exp(\beta) / QBY_0^n$ ], dimensionless
- $\delta$  Radiant absorption parameter [ $\delta = \gamma \Gamma \lambda_2 \mu T_0 / \Gamma_2 \dot{q}(\gamma+1)$ ], dimensionless
- $\theta$  Dimensionless surface temperature ( $\theta = T_s - T_0 / T_0$ )
- $\lambda$  Coefficient of thermal conductivity (cal/cm sec<sup>0</sup>K)
- $\mu$  Radiant absorption coefficient (cm<sup>-1</sup>)
- $\rho$  Density (gm/cm<sup>3</sup>)
- $\tau$  Dimensionless time  $\{\tau = \pi [q + QBY_0^n \exp(-E/RT_0)]^{1/2} t / \Gamma^2 T_0^2\}$
- $\Gamma_1$  Gas phase thermal responsivity [ $\Gamma_1 = (\lambda_1 \rho_1 C_1)^{1/2}$ ]  
cal/cm<sup>2</sup> deg K sec<sup>1/2</sup>
- $\Gamma_2$  Solid phase thermal responsivity [ $\Gamma_2 = (\lambda_2 \rho_2 C_2)^{1/2}$ ]  
cal/cm<sup>2</sup> deg K sec<sup>1/2</sup>
- $\Gamma$  Total responsivity ( $\Gamma = \Gamma_1 + \Gamma_2$ )

## SUBSCRIPTS

- 1 Gas phase (except as noted in text)
- 2 Solid phase (except as noted in text)
- \* Ignition conditions
- s Surface
- c Cutoff
- o Initial
- $\infty$  Far from surface

## 1. INTRODUCTION

Heterogeneous reactions have been proposed as the controlling mechanism in the ignition of solid propellants (Ref. 1). In Ref. 2, an extensive review is given of the status of ignition theory in which it is noted that, in the case of heterogeneous theory, there were at that time (1966) no published results of numerical solutions of the equations representing heterogeneous ignition, either with or without external heating. Williams (Ref. 3) later published an analysis accounting for external heating; in effect, his work could be considered a study of hypergolic ignition. The purpose of this paper is to extend the preceding analysis (1) by including the effect of subsurface absorption of external radiant flux, (2) by including the effect of unequal initial temperatures of the solid and gas phases, and (3) by presenting solutions for heating of an opaque solid propellant by a combination of surface chemical heating and a continuous or interrupted external stimulus. The solutions will be examined in the light of several arbitrary definitions of ignition in order to establish the conditions under which the choice of ignition criterion may or may not be important.

## 2. MATHEMATICAL MODEL

We consider the transient, one-dimensional system of Fig. 1, in which the solid propellant occupies the half-plane  $x < 0$  and the gaseous oxidizer occupies the half-plane  $x > 0$ . Initially, the propellant and oxidizer are at the uniform initial temperatures  $T_{2\infty}$  and  $T_{1\infty}$ , respectively. At time zero, the gaseous oxidizer of uniform mass fraction  $Y_0$  is brought into contact with the propellant. Simultaneously, a flux of constant magnitude  $q$  cal/cm<sup>2</sup> sec is turned on and illuminates the interface continuously or for a definite period of time, being absorbed by the solid according to an exponential decay law. The temperatures at a great distance into the solid and gas are maintained at  $T_{2\infty}$  and  $T_{1\infty}$ , respectively, while the oxidizer mass fraction at a great distance from the interface is maintained at  $Y_0$ . In addition to the external heating, chemical heating is generated at the interface according to a one-step irreversible reaction governed by an Arrhenius dependence on surface temperature.

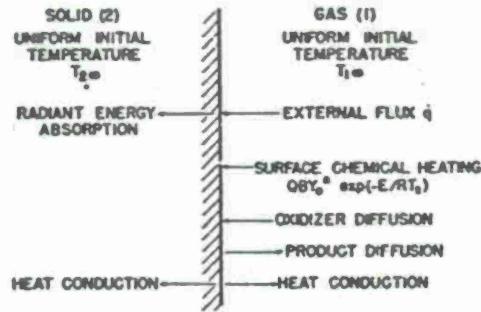


FIG. 1. Schematic Representation of Ignition with Surface Reaction and External Flux.

At  $t > 0$ , the processes which occur include: (1) heat exchange between the interface and the solid and gas phases, (2) diffusion of oxidizer to the surface, (3) surface chemical reaction between gaseous oxidizer and solid fuel, and (4) diffusion of products from the surface. The following governing equations for this system are derived from general conservation laws and constitutive relationships (see, e.g. Ref. 4):

Gas Phase ( $x > 0$ )

$$\text{Energy: } \rho_1 (\partial h_1 / \partial t) = \partial [(\lambda_1 / C_1) (\partial h_1 / \partial x)] / \partial x \quad (1)$$

$$\text{Mass: } \rho_1 (\partial Y / \partial t) = \partial [\rho_1 D (\partial Y / \partial x)] / \partial x \quad (2)$$

Solid Phase ( $x < 0$ )

$$\text{Energy: } \rho_2 (\partial h_2 / \partial t) = \partial [(\lambda_2 / C_2) (\partial h_2 / \partial x)] / \partial x + \mu \dot{q} \exp(\mu x) \quad (3)$$

Boundary ( $x=0$ )

$$\text{Temperature: } T_1 = T_2 \text{ or } h_1 / C_1 = h_2 / C_2 + T_{20} - T_{10} \quad (4)$$

$$\text{Energy: } (\lambda_2 / C_2) (\partial h_2 / \partial x) - (\lambda_1 / C_1) (\partial h_1 / \partial x) = Q_0 \rho_1 D (\partial Y / \partial x) \quad (5)$$

$$\text{Mass: } \rho_1 D (\partial Y / \partial x) = B Y^n \exp(-E/RT_s) \quad (6)$$

Initial ( $t=0$ )

$$h_1 = 0; h_2 = 0; Y = Y_0 \quad (7)$$

Asymptotic

$$h_1(\infty) = 0; h_2(-\infty) = 0; Y(\infty) = Y_0 \quad (8)$$

The assumptions made in deriving the foregoing equations are: (1) constant pressure, (2) neglect of thermal diffusion or diffuso-thermal effects, (3) neglect of external force fields such as gravity, electric, or magnetic, (4) adequacy of the use of binary diffusion coefficients, (5) negligible viscosity, (6) constant specific heats in each phase over the temperature range encountered, and (7) no surface regression during the ignition transient. Assumption (6) leads not only to the energy form of Eq. 4 but to the use of Eq. 1 without the need to assume a Lewis number of unity. Assumption (7) implies the absence of convective effects in the gas phase and further allows the extent of the reaction to be expressed in terms of the single variable  $Y$ .

Two noteworthy features of Eq. 1-8 are that (1) the only nonlinearity occurs in Eq. 6, a boundary condition, and (2) the enthalpy occurs explicitly only in boundary conditions, appearing only in differential form in the field equations. As a result, the surface temperature history is a function only of initial surface conditions (at  $t=0^+$ ) in addition to system parameters<sup>1</sup>. Following the technique of Williams (Ref. 3), one may transform Eq. 1-8 to the following dimensionless nonlinear integral equation for surface temperature vs time<sup>2</sup>:

$$\theta = \frac{1}{\pi} \int_0^{\tau_c} \frac{G(\theta, \lambda) d\lambda}{\sqrt{\tau-\lambda}} + \frac{1}{\pi} \int_{\tau_c}^{\tau} \frac{H(\theta, \lambda) d\lambda}{\sqrt{\tau-\lambda}} + \frac{\gamma}{\delta(\gamma+1)} [F(\tau) - F(\tau-\tau_c)] \quad (9)$$

where

$$G(\theta, \lambda) = \frac{1}{\gamma+1} \left\{ \gamma + \left[ 1 - \alpha\theta + \frac{2\alpha}{\pi} \frac{\gamma}{\gamma+1} \sqrt{\lambda} + \frac{\alpha}{\delta} \frac{\gamma}{\gamma+1} F(\lambda) \right]^n \exp(\beta\theta/1+\theta) \right\} \quad (10)$$

$$H(\theta, \lambda) = \frac{1}{\gamma+1} \left\{ 1 - \alpha\theta + \frac{2\alpha}{\pi} \frac{\gamma}{\gamma+1} (\sqrt{\lambda} - \sqrt{\lambda-\tau_c}) + \frac{\alpha}{\delta} \frac{\gamma}{\gamma+1} [F(\lambda) - F(\lambda-\tau_c)] \right\}^n \exp(\beta\theta/1+\theta) \quad (11)$$

<sup>1</sup> Temperature distribution is of course dependent on the remote boundary conditions; however, we shall be interested only in the surface which is assumed to be the sole reaction site.

<sup>2</sup> Three additional assumptions are made in this transformation, viz., the constancy of the groups,  $\rho_1^2 D$ ,  $\rho_1 \lambda_1 / C_1$ , and  $\rho_2 \lambda_2 / C_2$  with respect to temperature changes. The first two (gas phase) are practically constant at ambient temperatures for many compounds and vary inversely with cube root of absolute temperature at elevated temperatures. The solid phase parameter remains essentially constant over the temperature range of interest.

$$F(\lambda) = \exp(\delta^2 \lambda / \pi) \operatorname{erfc}(\delta \sqrt{\lambda} / \pi) - 1 \quad (12)$$

For convenience in considering the cases of interrupted heating, the roles played by  $\theta$  and  $\tau$  were interchanged from Ref. 3 so that now  $\tau$  is the independent variable. The parameter  $\alpha$  is a measure of the relative importance of heat and mass diffusions with a value of zero representing infinite mass diffusion;  $\beta$  is the dimensionless activation energy;  $\gamma$  is the ratio of external heating rate to initial chemical heating rate; and  $\delta$  is proportional to  $\mu$ , the absorption coefficient.

Although a computer program was written to solve Eq. 9-12, only the case of total surface absorption ( $\delta = \infty$ ) has been considered in the parameter study. The terms involving  $\delta$  vanish for this case. In the cases of interrupted heating,  $\tau_c$  is the dimensionless cutoff time. For continuous heating,  $\tau_c$  is set equal to  $\tau$  so that only the first integral in Eq. 9 remains. Complete definitions of the mathematical symbols are given in the nomenclature.

In Eq. 10, the expression in curly brackets represents the total heating rate,  $\gamma$  being the applied external rate with the remaining terms accounting for chemical heating. The entire function  $H(\theta, \lambda)$  represents chemical heating after shutoff of external flux.

### 3. QUALITATIVE BEHAVIOR

The general nature of the surface temperature history depends upon the relative importance at each instant in time of the constant applied external flux and the variable surface chemical heating. Figure 2 illustrates all the characteristics which may occur in the temperature-time curve. The points indicated by "1" are first inflection points. When  $\gamma=0$ , this point is a manifestation of the increasing reaction rate with temperature before diffusional effects limit the concentration. When  $\gamma>0$ , the first inflection represents the occurrence of significant chemical reaction relative to external heating. The point marked "2" represents the instant when chemical and external heating rates are equal. (It is absent when  $\gamma=0$  and occurs at  $\tau=0$  when  $\gamma=1$ ). The temperature under these conditions is readily calculated when  $\alpha=0$  by equating the chemical heating rate to the external heating rate in Eq. 10. Then

$$\theta_{\gamma} = \ln \gamma / (\beta - \ln \gamma) \quad (13)$$

From Eq. 13, it is seen that there are combinations of heating rate and activation energy for which the chemical heating cannot become dominant, viz.,  $\beta < 1/\gamma$ . The underlying basis for this behavior is the asymptotic form of the Arrhenius function so that the limitation indicated by Eq. 13, while relevant only for quite low activation energies (ca. 4 kilo-calories per mole) when  $\alpha=0$ , becomes of increasing importance for low diffusion rates (high  $\alpha$ ).

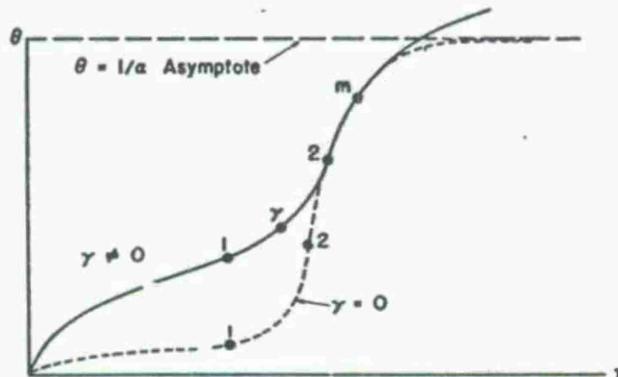


FIG. 2. Schematic Heating Curve for Surface Temperature with and without External Flux.

The points marked "2" in Fig. 2 are second inflection points where the effect of decreasing concentration on chemical reaction rate begins to be important. Second inflection points occur, albeit at unrealistically high temperatures, even when  $\alpha=0$  because of the asymptotic nature of the Arrhenius function. The opposing effects of increasing temperature and decreasing concentration ultimately lead to a maximum in the reaction rate (except when  $\alpha=0$ ) which is denoted by "m" and follows the second inflection point. The remaining characteristic is the asymptotic value of surface temperature for the cases  $\gamma=0$  and  $\alpha \neq 0$ . This behavior has been noted and explained in Ref. 2 and 3 and represents a balance between surface reaction rate and mass diffusion rate.

### 3.1 HYPERGOLIC CASES ( $\gamma=0$ )

Figure 3 depicts schematically the effect of  $\alpha$  and  $\beta$  on temperature-time curves for hypergolic heating ( $\gamma=0$ ). The time scale is different but uniform for each curve in order to illustrate the effect of  $\alpha$  and  $\beta$  on the shape of the  $\theta$  vs  $\tau$  curve for a wide range of parameters. High activation energies (large  $\beta$ ) and/or high mass diffusivities are typified by long induction periods followed by a rapid rise in temperature (curves A-C). As the activation energy decreases, the temperature-time curve gradually loses this two-stage characteristic (curves D and E); the inflection points vanish (curves F-H); and, in the limiting case of zero activation energy, the dimensionless surface temperature rises smoothly to a value of  $1/\alpha$ . Lower mass diffusivities promote this observed transition at higher activation energies.

### 3.2 CONTINUOUS EXTERNAL HEATING ( $\gamma \neq 0$ )

The effect of superimposing a constant external flux upon the variable chemical flux can be argued qualitatively even though the nonlinearity or

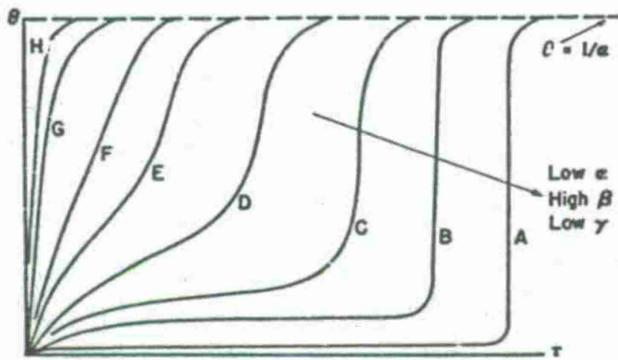


FIG. 3. Schematic Surface Temperature Histories Showing Effect of Parameters for Non-zero Values of  $\alpha$ .

the problem precludes any true mathematical superposition. As the intensity of external heating increases, the precipitous nature of the curves becomes less evident; the point of equal heating rates is no longer reached; the inflection points disappear and only the point of maximum chemical activity remains, shortly before depletion of the oxidizer. This transition with increasing external heating is represented by the series of curves in Fig. 3 except for the upper ends of the curves, which continue to increase with time after depletion instead of approaching the asymptote  $1/\alpha$  as in the hypergolic case.

### 3.3 INTERRUPTED EXTERNAL HEATING ( $\gamma \neq 0$ )

Figure 4 illustrates typical surface temperature vs time curves when the external flux is interrupted. Curve A represents shutoff at a time before chemical heating has become appreciable, either because of (1) insufficient heating time, (2) low diffusion rates and consequent early depletion, or (3) low activation energy and high external heating rate. In curve B, the heating curve has already deviated from that for an inert solid but as yet insufficient heat is being generated to sustain the reaction after shutoff. Curve C typifies shutoff at a time when chemical heating has become at least equal to external heating. Indeed a usually necessary condition for the occurrence of an increasing temperature soon after flux shutoff is the attainment of equal chemical and external heating rates. The requirement is unnecessary when the activation energy is low, the mass diffusion rate is high, and  $\ln \gamma$  is near its upper limit of  $\beta$ , since under these conditions, the knee of the Arrhenius curve and its effect on rate of temperature rise occur at a relatively low temperature. The requirement is insufficient in that if the shutoff temperature exceeds  $1/\alpha$ , the temperature either decays slowly toward  $1/\alpha$  (curve D) or, when the overheating is severe, drops rapidly and recovers after a relatively long time (curve E).

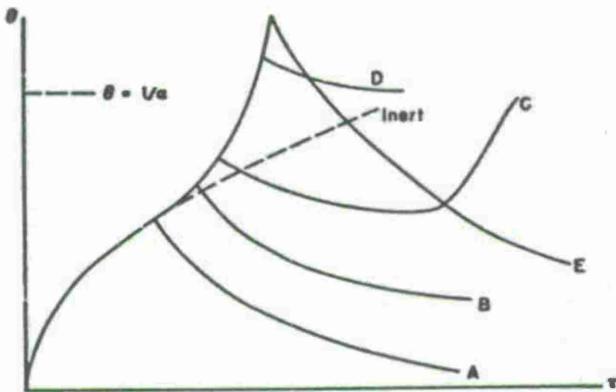


FIG. 4. Schematic Surface Temperature Histories for Interrupted External Heating and Finite Mass Diffusion ( $\alpha \neq 0$ ).

#### 4. SOLUTION AND RESULTS

Equations 9-12 were solved by an iterative finite difference technique on the Univac 1108 with automatic plotting of the  $\theta$  vs  $\tau$  curves on the Stromberg Carlson Plotter Model 4060. A parameter study covering the following range of parameters was carried out:

$$\begin{aligned}\alpha &= 0, 0.1, 1.0, 5.0, 10.0 \\ \beta &= 10, 20, 30, 50 \\ \gamma &= 0 - 10^{10} \\ \delta &= \infty \\ n &= 0 \text{ (equivalent to } \alpha=0 \text{) and } 1\end{aligned}$$

##### 4.1 INFINITE DIFFUSION RATE ( $\alpha=0$ )

Results are displayed in dimensionless form in Fig. 5 for various aspects of the continuous heating curves with  $\alpha=0$  and  $n=1$ . The solid curves show the time of equal chemical and external heating rates as a function of the parameters  $\beta$  and  $\gamma$ .<sup>3</sup> As commented previously, the curves have an upper vertical asymptote given by

$$\gamma = \exp(\beta) \quad (14)$$

<sup>3</sup> Curves representing intermediate values of  $\beta$  may be constructed in Fig. 5 by linear interpolation in the horizontal direction with respect to  $\beta$ .

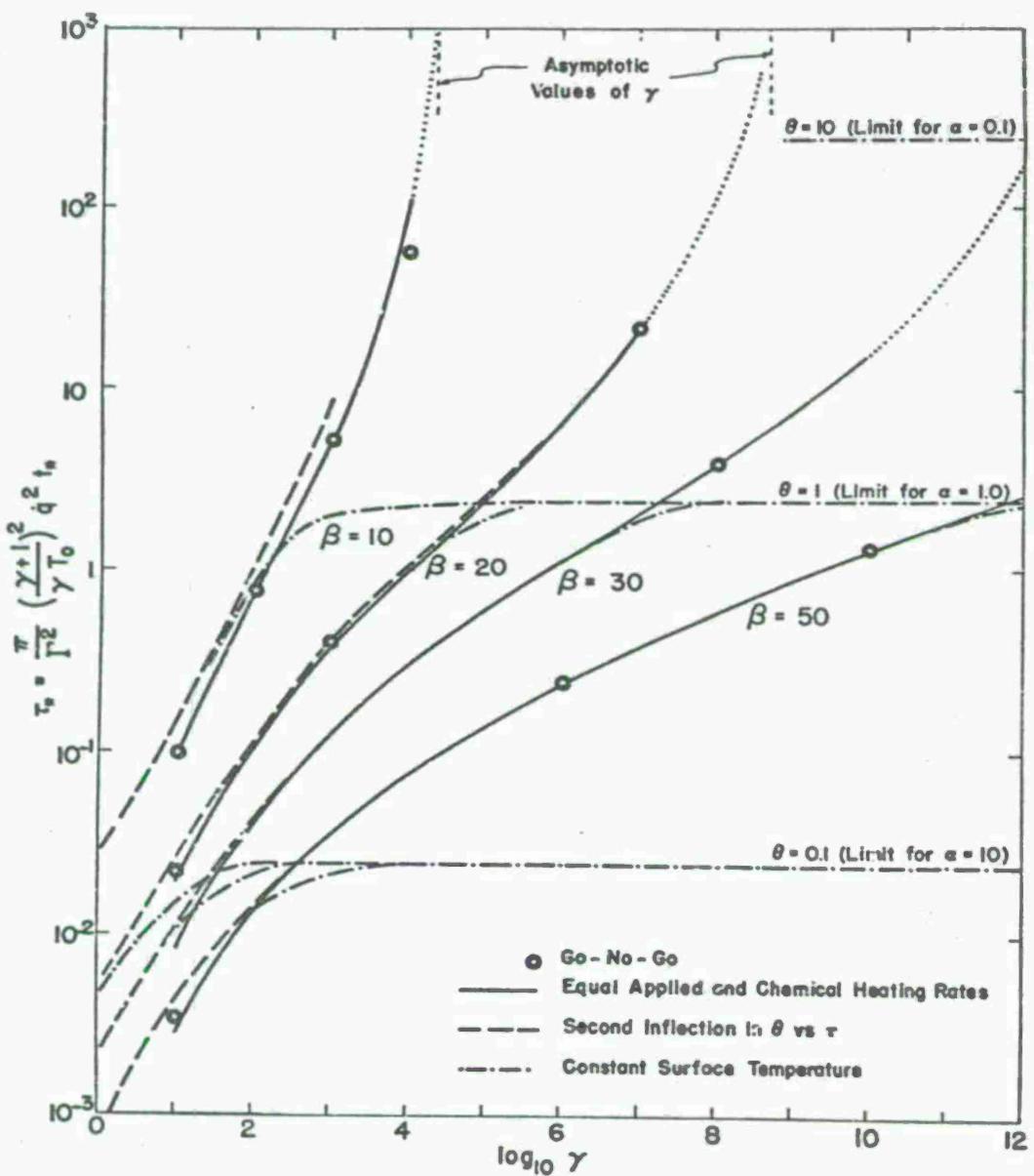


FIG. 5. Solutions for Heterogeneous Ignition Model with Infinite Mass Diffusion Rate.

which is indicated in the figure for low values of  $\beta$ . As previously remarked, equal chemical and external heating rates occur at  $\tau=0$  when  $\gamma=1$ . Hence, on the logarithmic scale used in Fig. 5, all curves (solid) representing this aspect of the temperature history are asymptotic to  $\log \gamma=0$ . The dashed lines represent the time corresponding to the second inflection point or the time at which the rate of temperature rise was so rapid that the computational scheme could not follow it without specification of an inordinately small time increment. The two sets of curves deviate from one another significantly only at low external heating rates and low activation energies. The broken curves represent equal values of  $\theta$ , the fractional rise in surface temperature above the initial interface temperature. For clarity, only a few values of  $\theta$  are shown. At high external heating rates the curves approach the same asymptotic value of  $\tau$  for all activation energies, a value given by the surface temperature of an inert system, viz.,  $\tau=(\pi\theta)^2/4$ , as obtained from Eq. 9-12 with large  $\gamma$ . This is to be expected because, with high heating rates, the contribution due to chemical reactions is no longer significant and the system appears inert. As the external heating rate decreases, the curves representing different constant temperatures for a given activation energy all coalesce with one another and with the curves representing precipitous temperature rise.

Points indicated by circles represent heating times for what are called go-no-go cases. These are typified by curve C in Fig. 4, for which the surface temperature after cutoff of external flux recovers (passes through a minimum) within a post cutoff time interval equal to the initial heating time. Representative calculations reveal that for  $\alpha=0$  the required heating time for go-no-go behavior lies between the points designated by  $\gamma$  and 2 in Fig. 2 (solid curve). Exceptions occur as  $\gamma$  approaches its upper asymptotic value as previously noted.

#### 4.2 FINITE DIFFUSION RATES ( $\alpha>0$ )

As the mass diffusion rate decreases, the quantitative results of the preceding section are modified in two ways. First, for the same values of  $\beta$  and  $\gamma$ , the values of  $\tau$  are increased by an amount up to 10%, the maximum effect occurring at low external heating rates, low activation energies, and low diffusion rates. Under such conditions the cutoff time has less effect on the form of the post cutoff temperature histories, so that the go-no-go criterion becomes less definite. The effect of increasing  $\alpha$  is to shift upward the curves representing equal heating rates and second inflection points by relatively the same amount without significantly changing the spread between them. Upper asymptotic values of constant temperature curves are not altered; only the lower portions are affected where they join the curves representing second inflection points.

The second and most dramatic effect of low mass diffusion rates is the manner in which the solid curves in Fig. 5 are truncated so that only the lower sections remain. Qualitatively, the curves for a given value of  $\beta$  (activation energy) end when  $\tau$  corresponds to a temperature greater than  $1/a$ . Since constant temperature curves are shown, the approximate upper limit of  $\tau$  is readily established for a given value of  $a$ . The horizontal portions of the constant temperature curves are given by  $\tau_{lim} = (\pi/2a)^2$ . Owing to the relationship between go-no-go behavior, second inflection point, and point of equal heating rates, this second limitation greatly reduces the range of parameters over which go-no-go behavior is observed.<sup>4</sup>

#### 4.3 HYPERGOLIC CASES ( $a=0$ )

Hypergolic heating represents not only the limiting situation with no external heating, but also is the condition under which the mass diffusion has its largest influence on various aspects of the heating curves. Owing to the logarithmic scale employed in Fig. 5, zero external heating cannot be represented. These cases are shown graphically in Fig. 6 for diffusion parameters in the range 0 to 5 and for second inflection points ( $\tau_2$ ) and constant temperature ( $\theta$  curves). The values of  $\tau$  for  $\beta=0$ , obtainable analytically for a given  $\theta$  (see Ref. 2, Eq. A24) are used as an aid in extrapolating the constant  $\theta$  curves to  $\beta=0$ . In the present notation, the cited equation becomes  $a\theta=1-\exp(a^2\tau/\pi)\operatorname{erfc}(a^2\tau/\pi)^{1/2}$ . For the slow mass diffusion rate exemplified by  $a=10$ , the relationship of surface temperature vs time exhibits no second inflection point except for activation energy parameters ( $\beta$ ) greater than 50.

#### 5. RELEVANCE TO PROPELLANT IGNITION

In the foregoing sections of the report, attention has been focused upon formulating, solving, and describing a model in which heterogeneous (interface) chemical reactions, augmented by an external interruptible energy flux, determine the surface temperature history. Granted the adequacy of the model, one is still faced with identification of a given heating curve as representing ignition or nonignition of a propellant. Mathematically, the choice is likely to be highly subjective, especially for situations in which the heating curve exhibits no outstanding singularities. Experimentally, the choice may be an impossible one because of the difficulty of relating experimental observations to points on the heating curve. Convenient experimental procedures include detection of light and pressure rise and the performance of go-no-go tests.

<sup>4</sup> The failure to attain a go-no-go situation is an artifact of the definition of go-no-go, since, if the surface temperature is raised above  $1/a$  during heating, it must decrease toward  $1/a$  (the asymptotic value) after shutdown.

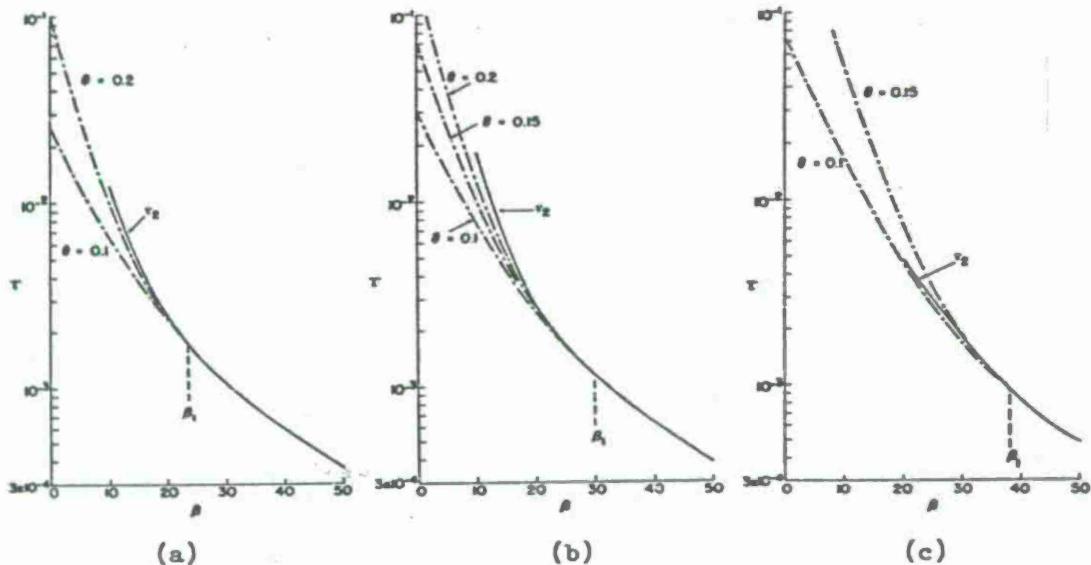


FIG. 6. Dependence of Dimensionless Hypergolic ( $\gamma=0$ ) Ignition Time upon Activation Energy ( $\beta$ ) and Diffusion Rate ( $\alpha$ ). (a)  $\alpha=0$  and  $0.1$ , (b)  $\alpha=1.0$ , (c)  $\alpha=5.0$ .

We shall avoid a resolution of the problem of defining ignition and instead shall examine the results of the mathematical solution of the model in the light of several commonly used, arbitrary choices. Specifically, we shall be interested in constant temperature, equal chemical and external heating rates, second inflection point, and go-no-go. We shall further wish to determine the conditions under which the definition of ignition is of minor importance.

### 5.1 CASES WITH EXTERNAL HEATING

For convenience in the ensuing discussion we designate ignition times based on ignition temperature as  $\tau_0$ , on equal chemical and external heating rates as  $\tau_y$ , on second inflection point as  $\tau_2$ , and on interrupted heating (go-no-go) as  $\tau_I$ . Reference to Fig. 5 reveals the existence of two regimes of external heating rate. In the low range, characterized by  $\gamma < 100$ , the various definitions of ignition lead in general to different ignition times according to the inequalities

$$\tau_y \leq \tau_I \leq \tau_2; \quad \tau_0 \leq \tau_2 \quad (\text{for realistic } \theta) \quad (15)$$

It is noted that  $\tau_y < \tau_2$  always, and that  $\tau_I$  is closer to  $\tau_y$  at low values of  $\beta$ . The relation of  $\tau_0$  in this scheme depends on the value of  $\theta$  chosen for the ignition criterion. In general,  $\tau_0$  increases with  $\theta$ , but the dependence becomes very weak as  $\beta$  increases and  $\gamma$  decreases. We

would expect this trend because these are just the conditions favorable to a precipitous rise in temperature. The effect of mass diffusion rate ( $\alpha$ ) complicates the above relations; no general statements can be made because of interactions of  $\alpha$ ,  $\beta$ , and  $\gamma$ .

When the external flux corresponds to  $\gamma > 100$ , the various ignition times become less distinct so that

$$\tau_\theta \leq \tau_\gamma = \tau_I = \tau_2 \quad (16)$$

An exception to Eq. 16 occurs as  $\gamma$  approaches  $\exp(\beta)$ . Then  $\tau_I < \tau_\gamma$  as indicated in Fig. 5 for  $\beta=10$ . When  $\gamma$  exceeds  $\exp(\beta)$ ,  $\tau_\gamma$  does not exist. The regime  $\gamma > 100$  may be further divided accordingly as: (a)  $\tau_\theta = \tau_\gamma$ ; (b)  $\tau_\theta < \tau_\gamma$ ; (c)  $\tau_\theta = \text{constant}$ . It is convenient in this regard to refer to two special values of  $\gamma$ . These are  $\gamma_1$ , below which  $\tau_\theta = \tau_\gamma$  (constant temperature lines merge with equal heating rate lines) and  $\gamma_2$ , above which  $\tau_\theta$  is constant (constant temperature lines are horizontal). Values of  $\gamma_1$  and  $\gamma_2$  are shown in Fig. 7 and 8 as functions of  $\theta$  and  $\beta$  for the

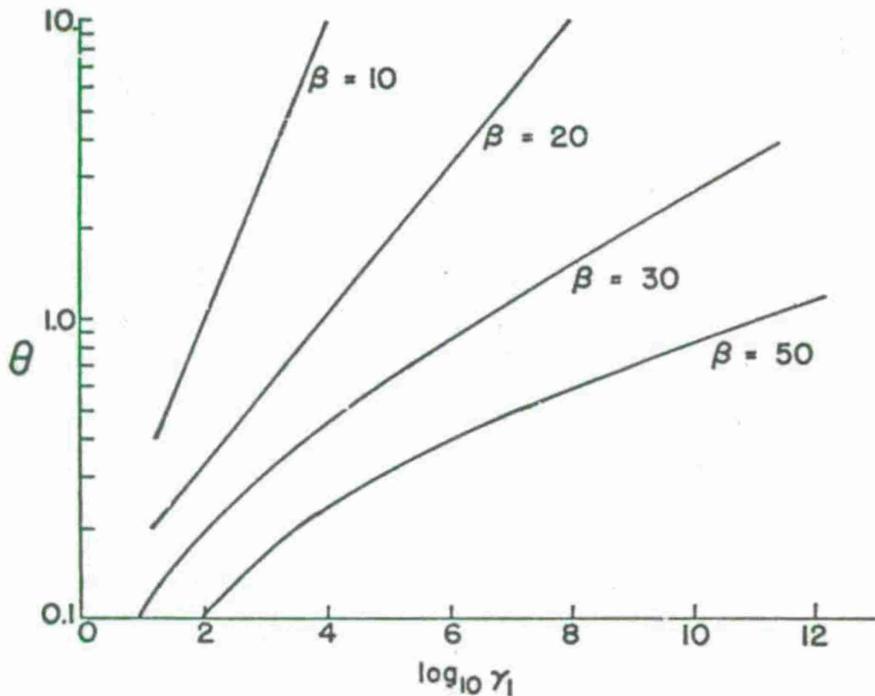


FIG. 7. Dimensionless Relationship Among Surface Temperature ( $\theta$ ), Activation Energy ( $\beta$ ), and  $\gamma_1$  (see text) for Infinite Mass Diffusion Rate ( $\alpha=0$ ).

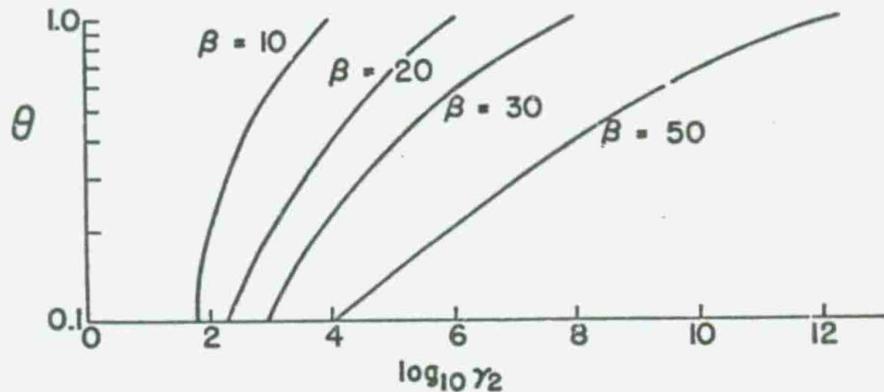


FIG. 3. Dimensionless Relationship Among Surface Temperature ( $\theta$ ), Activation Energy ( $\beta$ ), and  $\gamma_2$  (see text) for Infinite Mass Diffusion Rate ( $\alpha=0$ ).

case  $\alpha=0$ . The effect of  $\alpha$  is twofold as was noted in connection with Fig. 5. First, the curves of  $\gamma_2$  (and to a lesser degree, the curves of  $\gamma_1$ ) are shifted slightly to the left as  $\alpha$  increases. Second, the curves are truncated so that only the sections representing  $\theta < 1/\alpha$  remain. This means that in Fig. 7, the value of  $\gamma_1$  corresponding to given values of  $\alpha(=1/\theta)$  and  $\beta$  represents the highest external heating rate for which go-no-go ignition is observed.

Between  $\gamma=100$  and  $\gamma=\gamma_1$ , all the definitions of ignition considered here lead to virtually the same ignition time. This range is narrow for low  $\beta$  (activation energies) and low-mass diffusion rates (high  $\alpha$ ), vanishing completely for certain combinations of  $\alpha$  and  $\beta$  as inferred from Fig. 7. Under such conditions, if ignition is to be defined at all, it must be based on a critical ignition temperature, ignoring the inevitable effects of quenching by thermal and diffusional processes if the stimulating flux is terminated. Above  $\gamma=\gamma_2$ , the specification of a critical ignition temperature is tantamount to ignoring all chemical and diffusional processes and treating the propellant as inert.

## 5.2 CASES WITH NO EXTERNAL HEATING (HYPERGOLIC)

In the absence of external flux, the times  $\tau_Y$  and  $\tau_I$ , are no longer applicable and the ignition time must be based on the second inflection point or a critical temperature. Moreover, there is now a limiting value of surface temperature rise, given by  $\theta=1/\alpha$ . Hence, for low diffusion rates (high  $\alpha$ ), the surface temperature is limited to a relatively low value. Even the adoption of a critical rate of rise of surface temperature as ignition criterion cannot resolve the difficulty in this instance

because the maximum rate occurs at zero time. The relationships between  $\tau_0$  and  $\tau_2$  are shown in Fig. 6 for various combinations of  $\alpha$ ,  $\beta$ , and  $\theta$ . As noted above, values of  $\theta > 1/\alpha$  are not attainable. It is seen that  $\tau_0$  increases with  $\theta$ , the effect being greatest for small values of  $\beta$  and large values of  $\alpha$ . The value of  $\tau_2$  may be greater or less than  $\tau_0$  in contrast to cases with external heating because the second inflection point frequently occurs at low surface temperatures in the hypergolic case. The values of  $\tau_0$  and  $\tau_2$  approach one another as  $\beta$  increases; hence, hypergolic ignition may be equally well defined by some critical temperature (any value  $< 1/\alpha$ ) or second inflection point at higher activation energies exceeding the value  $\beta_1$ , a function of  $\alpha$  as shown in Fig. 6.

## 6. INTERPRETATION AND IMPLICATIONS OF RESULTS

It has been shown that the definition of ignition influences ignition time depending upon the range of parameters involved. Comparison has been made in terms of certain dimensionless parameters and variables which were convenient in the numerical solution of the problem. The results, displayed in Fig. 5 and 6 may be indicated functionally by the general relation:

$$\tau_* = f(\alpha, \beta, \gamma, n, \text{Def}) \quad (17)$$

or in dimensional form

$$\pi [q + QBY_0^n \exp(-E/RT_0)]^2 t_* / \Gamma^2 T_0^2 = \\ f[\Gamma T_0 / \rho_1 D^{1/2} QY_0, E/RT_0, q \exp(E/RT_0)/QBY_0^n, n, \text{Def}] \quad (17a)$$

where Def denotes dependence on definition of ignition. It is immediately obvious that such interesting physical quantities as  $q$ ,  $Y_0$ ,  $Q$ ,  $B$ ,  $E$ , and  $D$ , as well as pressure (which enters through  $\Gamma$ ,  $\rho$ ,  $B$ ,  $D$ , and, under certain conditions,  $T_0$ ) are involved in a complicated manner. Moreover, it is not possible, by the choice of any other single set of dimensionless groups, to decouple all the physical quantities whose effect is desired. In this section the effects of mass fraction, thermal properties, and external heating rate will be examined by the use of Fig. 5 and 6 and the requisite additional graphical relations. The discussion will be in terms of the magnitude of external heating and the ignition criterion. The more complicated effect of pressure will be dealt with separately.

## 6.1 EFFECTS OTHER THAN OF PRESSURE

6.1.1 Hypergolic Ignition ( $\gamma=0$ )

Under conditions of no external heating, only two meaningful ignition criteria remain of the ones previously discussed, viz., the second inflection point,  $t_2$ , and constant temperature,  $\tau_0$ . Equation 17a simplifies to

$$\pi [QBY_0^n \exp(-E/RT_0)/RT_0]^2 t_* = f[RT_0/\rho_1 D^{\beta/2} QY_0, E/RT_0, \text{Def}] \quad (18)$$

This relationship is shown graphically in Fig. 6 for  $n=1$ . The effect of  $n$  is second order for  $\alpha < 5$  and  $\beta > 20$ . The function "f" in Eq. 18 is given empirically within 5% by

$$f = f_1 (E/RT_0)^{f_2} \quad (19)$$

where  $f_1$  and  $f_2$  are two functions of  $\alpha$  shown below.

$\alpha$	$f_1$	$f_2$
0, .1	2.3	-2.23
1	5.0	-2.44
5	6.9	-2.44

At constant  $E/RT_0$ ,  $t_2$  changes by less than a factor of 2 over the range of values of  $\alpha$  investigated. Ignoring this variation compared to order of magnitude effects allows us to conclude that

$$t_2 \propto (RT_0/QBY_0^n)^2 (E/RT_0)^{2.3} \quad (20)$$

The effect of  $\alpha$  would be to increase the exponent of the first factor of Eq. 20 very slightly.

If ignition is defined by the constant temperature criterion,  $\tau_0$  is given by Eq. 20 where  $\beta > \beta_1$ . When  $10 < \beta < \beta_1$ , for meaningful temperature rises represented by  $\theta > 0.2$ ,  $\tau_0$  differs by no more than 30% from the value given by Eq. 20. Under no conditions can ignition occur under this criterion if  $\theta_{\text{ign}} > 1/\alpha$ .

6.1.2 Ignition with External Heating ( $\gamma > 0$ )

The discussion of ignition with external heating will be limited to the practical range  $\gamma > 100$ , thereby serving the following useful purposes:

- (1) Only two of the ignition criteria need be considered, viz., constant temperature and go-no-go.

(2) The chemical heating term relative to  $\dot{q}$  on the left side of Eq. 17a is negligible.

(3) The effect of  $\alpha$  may be ignored except as it establishes limiting conditions.

(4) The direct effect of "n" in solving Eq. 9-12 (not its effect in  $Y_0^n$ ) may be ignored.

Figures 9, 10, and 11 are derived from Fig. 5 and are included to show the individual effects of several physical parameters. Figure 9 emphasizes primarily the effect of external heating rate on ignition time. In order to clarify the presentation, only a limited number of constant temperature curves are displayed. The trend in general follows the one set in solid phase thermal theory in which higher surface temperatures are required for ignition at higher external heating rates. Between  $\gamma=100$  and  $\gamma=\gamma_1$  there is little to distinguish ignition times defined by go-no-go and constant temperature; the relationship followed is

$$t_* \propto \dot{q}^{-a} \quad (21)$$

where "a" is a weak function of  $\dot{q}$  and  $\beta$ , and is given over a wide range of parameters by

$$a = 2 - (8.4/\beta) \quad (22)$$

As  $\gamma$  decreases toward 100 or increases toward  $\exp(\beta)$ , "a" is significantly lower than predicted by Eq. 22. Above  $\gamma=\gamma_1$ , go-no-go ignition times continue to follow Eq. 21 subject to the stated limitations, while ignition times based on constant temperature above  $\gamma=\gamma_2$  are given by

$$t_* = \pi r^2 (T_* - T_0) / 4q^2 \quad (23)$$

It is emphasized that  $\gamma_1$  and  $\gamma_2$  depend upon  $\beta$  and  $\theta$ , the critical temperature chosen for the constant temperature criterion. Equation 23 is the classical expression for ignition time of an inert solid based on constant ignition temperature  $T_*$  (Ref. 2).

Figure 10 depicts the effect of  $Q$ , the heat of reaction,  $B$ , the rate coefficient, and  $Y_0$ , the initial mass fraction of oxidizer upon ignition time. At heating rates above  $\gamma_2$ , the constant temperature criterion predicts no effect of the group,  $QBY_0^n$ , while the relation for the go-no-go criterion becomes

$$t_* \propto (QBY_0^n)^{-b} \quad (24)$$

where

$$b = 8.4/\beta \quad (25)$$

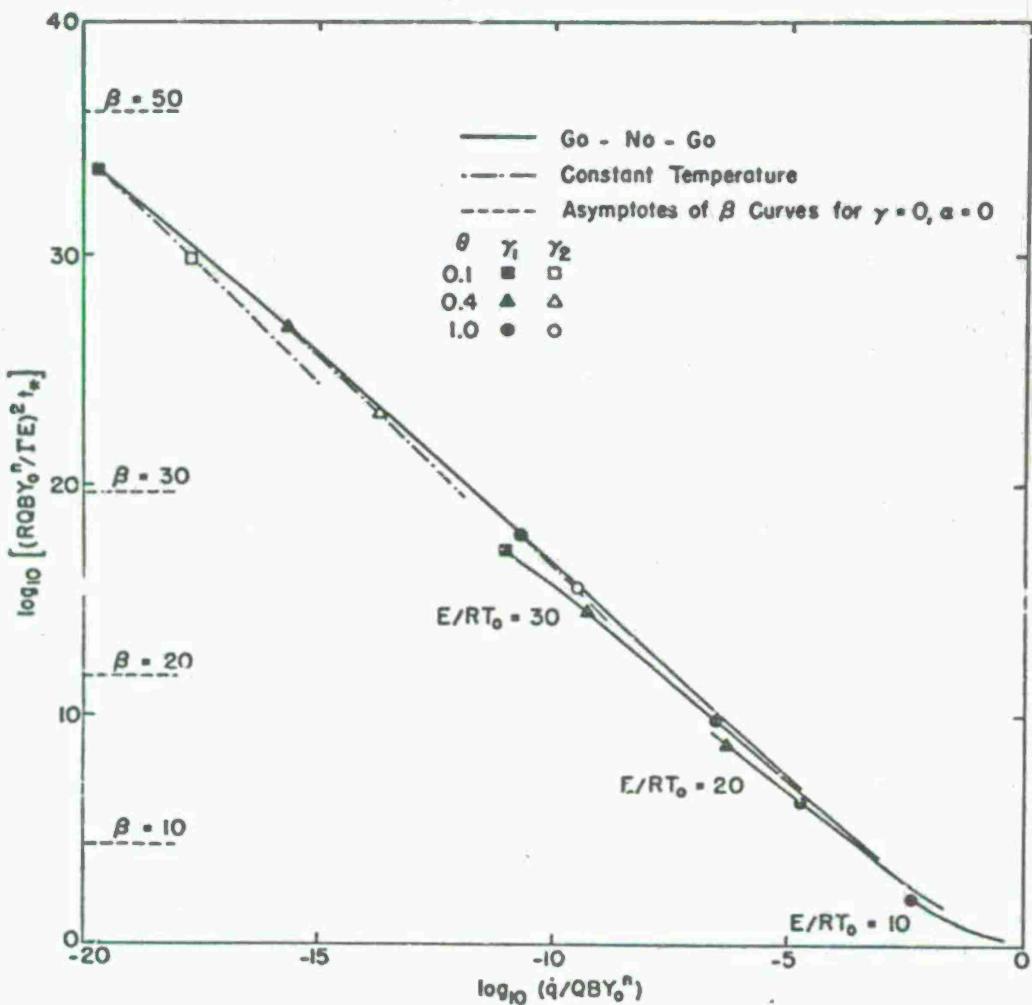


FIG. 9. Effect of External Heating Rate on Ignition Time  
(Constant Temperature and Go-No-Go Criteria).

Equations 22 and 25 are applicable over the same range of parameters. Hence, it is seen that ignition time given by the go-no-go criterion is less sensitive to  $Y_0$  for high activation energies, becoming slightly more dependent on  $Y_0$  at the extremes of heating rate. It should be noted that the ordinate scale factor in Fig. 10 contains the quantity  $\Gamma = (\lambda_1 \rho_1 c_1)^{1/2} + (\lambda_2 \rho_2 c_2)^{1/2}$ , the total responsivity of the gas and solid phases. At higher pressures (greater than ten atmospheres) the effect of oxidizer mass fraction on  $\Gamma$  should also be considered in studying how  $Y_0$  affects  $t_*$ . The exact results depend on the nature of the oxidizer and

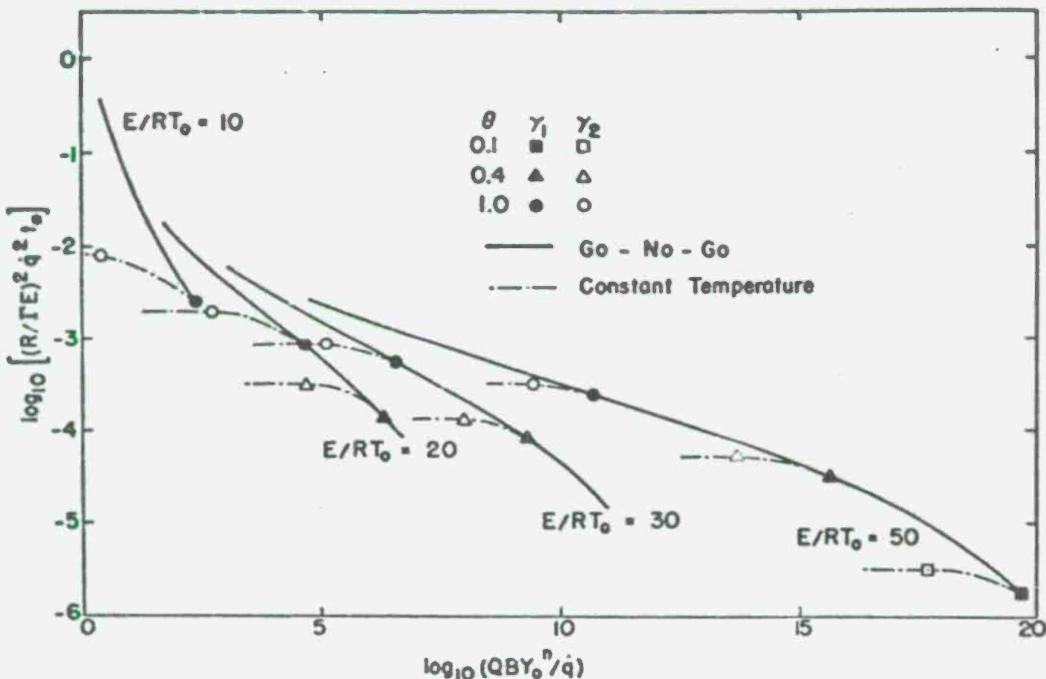


FIG. 10. Effect of  $QBY_0^n/q$  on Ignition Time (Constant Temperature and Go-No-Go Criteria).

inert diluent in the gas phase. It is also seen that initial surface temperature,  $T_0$ , has a powerful effect on ignition time, especially at high values of  $QBY_0^n/q$ . Figure 11 shows the importance of activation energy in determining ignition time.

#### 6.2 EFFECT OF PRESSURE

Ambient gas pressure influences the ignition phenomenon by three basic mechanisms:

(1) Effect on concentration of active species through the rate coefficient  $B$ , given by

$$B = v \rho_1^n = v(pM/RT_s)^n \quad (26)$$

The effect of  $T_s$  on  $B$  has been neglected relative to the effect of  $T_s$  in the Arrhenius factor of reaction rate.

(2) Effect on thermal losses by conduction to the gas as reflected in  $\Gamma$  and  $T_0$ .

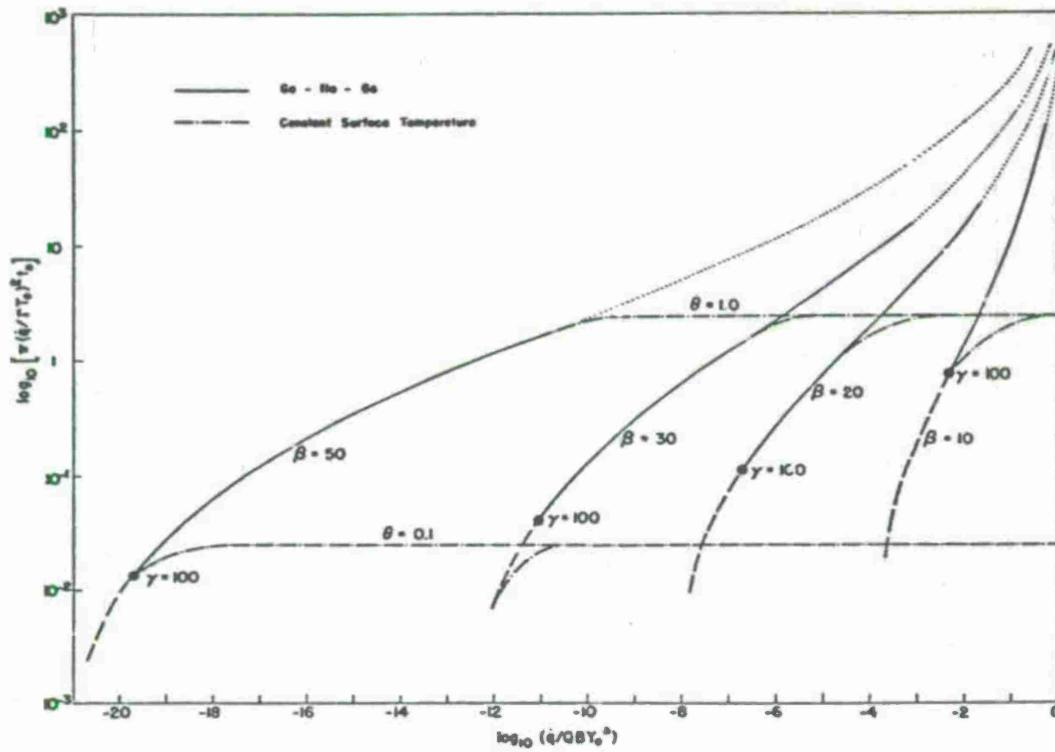


FIG. 11. Effect of Activation Energy on Ignition Time (Constant Temperature and Go-No-Go Criteria).

(3) Effect on diffusional processes in the parameter  $\alpha = \Gamma T_0 / \rho_1 D^{1/2} Q Y_0$ .

Mechanism (1) is of importance over the entire pressure range. At low pressures, it leads to the conclusion that ignition time depends upon oxidizer concentration, regardless of whether it is varied by changing the mass fraction or the total pressure.

The effect of mechanism (2) is obtainable from the expressions for  $\Gamma$  and  $T_0$ :

$$\Gamma = (\lambda_1 \rho_1 c_1)^{1/2} + (\lambda_2 \rho_2 c_2)^{1/2} \quad (27)$$

$$\Gamma T_0 = (\lambda_1 \rho_1 c_1)^{1/2} T_{1\infty} + (\lambda_2 \rho_2 c_2)^{1/2} T_{2\infty} \quad (28)$$

When the solid and gas phases are initially at the same temperature,  $T_{1\infty} = T_{2\infty}$ ; the initial surface temperature is then independent of thermal properties. If  $T_{1\infty}$  and  $T_{2\infty}$  are unequal,  $\Gamma$  and  $T_0$  both depend on thermal

properties; hence they depend on pressure. Incorporating the usual relations (Ref. 4) between pressure and gas transport properties leads to

$$\Gamma = K_1 p^{\frac{1}{2}} + K_2 \quad (29)$$

$$T_o = (K_3 p^{\frac{1}{2}} + K_4) / (K_1 p^{\frac{1}{2}} + K_2) \quad (30)$$

The quantitative effect of pressure on ignition time through the heat loss mechanism is obtainable by evaluation of  $K_1$ ,  $K_2$ ,  $K_3$ , and  $K_4$  for a particular situation, followed by use of the appropriate graphical or empirical relationship between  $\Gamma$ ,  $T_o$ , and ignition time.

The effect of pressure on diffusional processes appears only in the parameter  $\alpha$ ; hence, it would appear only in a limiting role under the go-no-go definition of ignition. Qualitative evaluation of this effect of pressure depends upon establishing the pressure dependence of each of the terms in the definition of  $\alpha$ , as well as the pressure dependence of the limiting value of  $\alpha$  as may be inferred from Fig. 7. The complicated nature of the relationships involved precludes any comprehensive study or general conclusions.

### 6.2.1 Hypergolic Ignition

The first order effects of pressure on hypergolic ignition time are obtainable from Eq. 20. Two cases are important, viz., equal or unequal initial temperatures of the gas and solid.

6.2.1.1 Equal Initial Temperatures. Here the value of  $T_o$ , the initial interface temperature, is pressure independent, so that

$$t_* \propto (K_1 p^{\frac{1}{2}} + K_2)^2 p^{-2n} Y_o^{-2n} \quad (31)$$

At low pressures it is clear that  $p$  and  $Y_o$  influence ignition time in nearly the same manner. Thus we have the often repeated statement that concentration changes affect the ignition time in the same manner, whether brought about by changes in pressure or mass fraction of the oxidizer. At higher pressures, the effects are not the same: the sensitivity of  $t_*$  to pressure changes is less owing to enhancement of heat loss to the gas phase at high pressures. For an effective zero order reaction, there would be no effect of changing the mass fraction, while ignition time would increase with increasing pressure.

6.2.1.2 Unequal Initial Temperatures. Under this condition we may write Eq. 20 as

$$t_* \propto (K_1 p^{\frac{1}{2}} + K_2)^2 T_o^{-3} p^{-2n} Y_o^{-2n} \quad (32)$$

Again the effects of pressure and mass fraction are similar at low pressures. At elevated pressures,  $T_o$  is dependent upon pressure. Two situations may be considered depending on whether the solid or gas is at a higher initial temperature.

(1)  $T_{1\infty} > T_{2\infty}$ . With a higher temperature in the gas,  $T_o$  increases with increasing pressure, leading to a greater dependence of  $t_*$  on pressure than was found in Section 6.2.1.1 above.

(2)  $T_{2\infty} > T_{1\infty}$ .  $T_o$  decreases with increasing pressure, so that the effect of pressure on ignition time is less than with equal initial temperatures.

### 6.2.2 Ignition with External Heating

Under conditions involving external stimulus, consideration must be given to the definition of ignition as well as to the relative temperatures of the solid and gas.

6.2.2.1 Equal Initial Solid and Gas Temperatures. The criterion of an ignition temperature (Eq. 23) leads to the result that, for  $\gamma > \gamma_2$ , changes of pressure in the low pressure regime do not affect ignition time. At high pressures, owing to greater heat loss, the ignition time increases with pressure. For the ignition temperature criterion and  $\gamma > \gamma_1$ , or for go-no-go and  $\gamma > 100$ , Fig. 10 may be applied in the form of the relation

$$t_* \propto (K_1 P^{\frac{1}{2}} + K_2)^2 (p/Y_o)^{-8.4nRT_o/E} \quad (33)$$

At low pressures, we again find that the influence of pressure and mass fraction on ignition time are similar, although the sensitivity is less than under hypergolic conditions. At high pressures, the effect of increasing pressure could conceivably result in increasing the ignition time, especially for reactions with high activation energies.

6.2.2.2 Unequal Initial Solid and Gas Temperatures. Equations 23 and 33 may also be applied for the temperature and go-no-go criteria, respectively, taking into account the dependence of  $T_o$  on pressure. Two situations arise, depending on the relative magnitude of  $T_{1\infty}$  and  $T_{2\infty}$ . We consider the high pressure regime.

(1)  $T_{1\infty} > T_{2\infty}$ . The initial interface temperature,  $T_o$ , increases with increasing pressure, leading to decreasing ignition times for both go-no-go and temperature criteria. The effect of pressure on the go-no-go ignition time is extremely great, however, owing to the exponential nature of  $T_o$  in Eq. 33.

(2)  $T_{2\infty} > T_{1\infty}$ . The initial temperature decreases with increasing pressure. The ignition time based on constant temperature increases with

increasing pressure while the effect on go-no-go time is indefinite depending on the relative effects of the two factors in Eq. 33.

## 7. SUMMARY

Results have been presented of computations on a mathematical model of solid propellant ignition in which constant external heating and surface chemical reactions provide the ignition stimulus. One of the reactants (oxidizer) is assumed to be initially present in the gas phase and to react with the solid fuel. Mass and heat diffusion and conduction are included in the analysis while surface regression is ignored during the ignition transient. The surface temperature history has been computed for the cases of continuous and interrupted application of external energy and for the hypergolic case with no external flux. A wide range of values of kinetic constants, diffusional parameters, and heating rates was studied. Several commonly used definitions of ignition have been examined in terms of the surface temperature history. These include: (1) attainment of a specified surface temperature, (2) attainment of a second inflection point in the curve of temperature vs time, (3) attainment of a condition in which chemical heating equals external heating, and (4) in cases of interrupted heating, the occurrence of a runaway surface temperature after shutdown, within a time interval equal to the initial heating period. All or none of these four characteristics of the heating curve were observed depending upon the set of physical parameters involved.

Under hypergolic conditions, only the first two definitions are relevant, becoming nearly equivalent for moderate to high activation energies and mass diffusion rates. For low mass diffusion rates, the maximum temperature rise is small, so that even the appearance of an inflection point in the temperature vs time curve is no assurance of physical ignition. For low to moderately high external heating rates, all four definitions lead to nearly equal ignition times; under extremely high external rates, the first definition results in the prediction of shorter ignition times. In addition, there exists an upper external heating rate above which the fourth definition does not lead to ignition at all. This limiting rate is an increasing function of mass diffusion rate and activation energy; however, when ignition occurs, ignition time is relatively insensitive to mass diffusion rate.

The effect of physical parameters and groups of parameters has been examined. In particular, owing to conclusions and claims of previous investigators, attention has been directed toward studying the effect of oxidizer concentration on ignition time. It was found that in the low pressure range, for both hypergolic and externally heated cases, ignition time is nearly the same, whether concentration is varied by changing the mass fraction of oxidizer or the total pressure. However, at higher pressures (exact value a function of the properties of materials involved),

the sensitivity of ignition time to changes in concentration depends upon how that change is brought about. The effect of pressure changes may be greater or less than changes in oxidizer mass fraction because of competing influences of pressure on reaction rate and heat loss.

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13. ABSTRACT Mathematical solutions are obtained for a model of solid propellant ignition by the combined action of external flux and surface reaction between a solid fuel and gaseous oxidizer with hypergolic ignition as the limiting case. Several commonly used definitions of ignition are examined and compared in the light of the surface temperature history. Conditions are established under which the definition of ignition can be expected to influence ignition time; major differences appear at high heating rates between the ignition times based on constant ignition temperature and on other criteria. The effect of oxidizer concentration on ignition time is investigated; at low pressures, the manner of variation of concentration is unimportant, while at high pressures, variations of mass fraction and pressure have different effects. Finally, it was found that chemical kinetics is the principal factor in determining ignition time, while mass diffusion rate imposes a limit on the attainment of ignition without significantly affecting ignition time. ( )			

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